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54 Catalytic process for preparing cyclohexanone-oxime.

57 A catalytic process for preparing cyclohexanone-oxime by reacting cyclohexanone with NH_3 and H_2O_2 in the liquid phase, wherein the catalyst substantially consists of a highly crystalline substance containing SiO_2 and having a zeolitic structure.

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CATALYTIC PROCESS FOR PREPARING CYCLOHEXANONE-OXIME

DE-C-1 245 371 teaches the preparation of cyclohexanoneoxime by catalytic reaction, in the liquid phase, of cyclohexanone with ammonia and hydrogen peroxide at 5 to 40°C. In the presence of a catalyst consisting of phospho-tungstic acid or of similar compounds. A drawback of this method is, however, that this type of catalyst is difficult to handle, particularly, during the separation of the product from the catalyst.

It has now been found that it is possible to obtain the same high yields by using a completely different catalyst that is easier to handle and simplifies the process in all its steps.

Thus, the present invention relates to a catalytic process for preparing cyclohexanone-oxime by reacting cyclohexanone with NH_3 and H_2O_2 in the liquid phase, which process is characterized in that the catalyst substantially consists of a highly crystalline, SiO_2 -containing substance having a zeolitic structure and, in particular, of a titanium-silicalite, optionally in admixture with an inert binder. Titanium-silicalites are known compounds which, for example, are described in GB-A-2 024 790 and 2 071 071.

The reaction temperature normally is in the range of from 25 to 100°C, preferably from 40 to 90°C. Tests carried out at 15°C have provided results that are not completely satisfactory.

A pressure above atmospheric pressure promotes the development of the reaction.

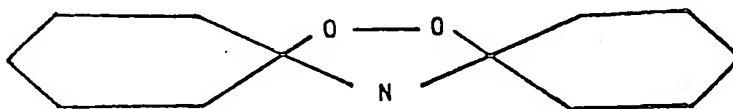
Other substances of zeolitic nature which catalyze the reaction are, first of all, the various types of silicalite, such as silicalite I (see, e.g., US-A-4 061 724), silicalite II, zirconium-silicalites and hafnium-silicalites.

Another class of analogous catalysts are the metasilicalites, e.g., borosilicates (boralites), beryll-silicates, chromo-silicates, vanadium-silicates, zirconium-silicates, gallium-silicates and ferro-silicates which are, in part, described in GB-A-2 024 790.

A third class of catalysts of analogous type consists of the known aluminium-silicates, generally known as "zeolites", particularly the zeolites of type Y, the zeolites ZSM5, the zeolites ZSM 11 and the other zeolites ZSM described in EP-A-129 239, 141 514 and 143 642, as well as the zeolites MB 28 described in EP-A-21 445. Some of these zeolites have already been successfully utilized in the aminoximation of cyclohexanone in the gas phase with NH_3 and air.

The process according to the present invention can be carried out either continuously or discontinuously, provided that reactors with surfaces that are resistant to hydrogen peroxide are used. When the reaction is carried out in batch, it is advisable that 0.1 to 50 parts by weight (preferably from 1 to 20 parts by weight) of pure catalyst (excluding binder) for 100 parts by weight of cyclohexanone be used. If the reaction is performed in a continuous manner, it is preferred to employ a space velocity of from 0.1 to 100 kg/h of cyclohexanone - ($\text{C}_6\text{H}_{10}\text{O}$) per kg of catalyst. The molar ratio of $\text{H}_2\text{O}_2:\text{C}_6\text{H}_{10}\text{O}$ is, generally, in the range of from 0.5 to 2.5 and, preferably, from 1 to 1.5, whereby H_2O_2 means 100% pure hydrogen peroxide (i.e., dilution water excluded). Water (H_2O) is the most suitable liquid vehicle for the reaction. However, it is also possible to use organic water-soluble solvents capable of dissolving both pure ammonia and its aqueous solutions such as, e.g., methanol, ethanol, propanol, isopropanol, butanol, isobutanol, tertiary butanol and mixtures thereof. Solvents with carbonyl functions such as aldehydes and ketones should be excluded.

The reaction water, which is formed according to the equation: $\text{C}_6\text{H}_{10}\text{O} + \text{H}_2\text{O}_2 + \text{NH}_3 \rightarrow \text{C}_6\text{H}_{10}\text{ONOH} + 2\text{H}_2\text{O}$ (I) gradually increases the amount of liquid vehicle as the conversion to oxime proceeds. During the reaction considerable amounts of peroxy-di-cyclohexyl-amine of the formula



(II)

are also formed.

Ammonia should always be added before the hydrogen peroxide and in excess ($\text{NH}_3:\text{C}_6\text{H}_{10}\text{O} \geq 1$, preferably ≥ 1.5 moles/mol). Otherwise, undesired side-reactions occur.

At the end of the reaction, the cyclohexanone-oxime can be separated by different methods, for example, through extraction with suitable solvents such as benzene, toluene and the cyclohexanone as used for the synthesis, whereby a hydrophobic organic phase and an aqueous phase are formed.

Cyclohexanone-oxime and unreacted cyclohexanone form the organic layer. The aqueous layer which contains the excess NH_3 as well as traces of cyclohexanone and oxime can be recycled to the reaction zone (ammoximation zone).

The following examples illustrate the invention without, however, limiting it.

EXAMPLE 1

A glass reactor, equipped with a stirrer and a heating jacket, was first blanketed with an inert gas (nitrogen). Subsequently, 1.5 g of a catalyst consisting of a finely ground powder of titanium-silicalite containing 3.85% by weight of highly crystalline titanium oxide (average diameter of the particles $\leq 5 \mu\text{m}$) was charged. 50 cm³ of a 32% by weight aqueous solution of ammonia were added to the catalyst. The mixture was stirred and 9.5 g of cyclohexanone were charged. The three-phase system (solid-aqueous-organic) formed was kept homogenous by stirring vigorously. Heating was started by conveying a liquid at 60°C into the jacket. Simultaneously, a 32% by weight aqueous solution of hydrogen peroxide was fed to the reactor by means of a metering pump. After 15 minutes, the temperature in the reactor reached 60°C while the pressure rose to a value of from 600 to 700 mm Hg above atmospheric pressure. The addition of H_2O_2 was performed within 3.5 hours, during which time the pressure decreased. The temperature was maintained at 60°C and stirring was continued for a further 1.5 hours, whereafter the test was stopped and the mixture was cooled.

50 cm³ of toluene were added to the resulting suspension and, after stirring for a few minutes, the aqueous phase and the organic phase were separated from the catalyst by filtration. The liquid phases were separated in a separation funnel and

the aqueous phase was extracted with two portions of toluene of 30 cm³ each. The toluene solutions were combined and analysed. The analysis revealed a cyclohexanone conversion of 95% and a selectivity to cyclohexanone-oxime of 79.45%; the selectivity of hydrogen peroxide to oxime was 68.7%. At the end, about 15% of the starting cyclohexanone was found to be in the form of peroxy-dicyclohexyl-amine (see formula II above).

EXAMPLES 2 and 3

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Example 1 was repeated, varying temperature and pressure. The data and results given in table 1 prove that the selectivity of the conversion $\text{H}_2\text{O}_2 \rightarrow$ oxime is very adversely affected when operating under vacuum.

EXAMPLE 4 (Comparative Test)

Example 1 was repeated, bringing the pressure (gauge) to zero and considerably lowering the temperature (down to 15°C). The unsatisfactory results shown in table 1 prove that it is disadvantageous to excessively reduce the thermal level of the ammoximation.

EXAMPLE 5

Example 1 was repeated, replacing titanium silicalite by a zirconite (zirconium-silicalite). Analogous results were obtained.

EXAMPLE 6

Example 1 was repeated, replacing titanium-silicalite by a borasilite (boron-silicate). Analogous results were obtained.

TABLE 1 (a)

Ex.	PARAMETERS					PRODUCTS							
	$C_6H_{10}O$ (g)	H_2O 32% b.w.	T (°C)	Time (h)	P (mmHg)	Liquid phase		Gas composition		Conversion (%)		Selectivity (%)	
						aqueous (g)	organic (g)	N_2O (vol.%)	O_2 (vol.%)	$C_6H_{10}O$	H_2O	$C_6H_{10}O$	H_2O
1	9.50	11.7	60	3 1/2	75	52.0	127	17.22	23.14	95.35	91.87	79.45	68.73
2	9.50	11.55	40	"	negative	50.8	114.5	-	-	90.37	79.20	30.97	25.74
3	9.50	11.7	25	"	0	57.0	120	0.335	95.49	82.56	98.13	20.53	15.37
4	9.55	11.8	15	3 3/4	0	71.3	91	0.094	69.07	47.79	95.48	16.70	7.22
(*)													

(*) Comparative test.

(a) In all the tests, 50 cm³ of aqueous NH_3 were added and 1.5 g of Ti-silicalite were used.

(b) Above atmospheric pressure.

(c) Selectivity to oxime.

Note : Nitrogen protoxide derives from the decomposition of hydroxylamine, which forms in consequence of a parallel reaction.

Claims

1. A catalyst process for preparing cyclohexanone-oxime by reacting cyclohexanone with ammonia and hydrogen peroxide in the liquid phase, characterized in that the catalyst substantially consists of a highly crystalline substance containing SiO_2 and having a zeolitic structure.

2. The process of claim 1, wherein the catalyst is a titanium-silicalite, optionally in admixture with an inert binder.

3. The process of claim 2, wherein a zirconium-silicalite replaces, at least in part, titanium-silicalite.

4. The process of claim 2, wherein a borasilite replaces, at least in part, titanium-silicalite.

5. The process of any one of claims 1 to 4, wherein the reaction temperature ranges from 25 to 100°C.

6. The process of claim 5, wherein the reaction temperature ranges from 40 to 90°C.

7. The process of any one of claims 1 to 6, wherein the pressure is equal to or higher than atmospheric pressure.

8. The process of any one of claims 1 to 7, wherein the space velocity of cyclohexanone ranges from 0.1 to 100 kg/h per kg of pure catalyst (binder excluded).

9. The process of any one of claims 1 to 8, wherein the $\text{H}_2\text{O}_2 : \text{C}_6\text{H}_{10}\text{O}$ molar ratio ranges from 0.5 to 2.5, whereby H_2O_2 means pure hydrogen peroxide (dilution water excluded).

10. The process of any one of claims 1 to 9, wherein NH_3 is added prior to H_2O_2 , the $\text{NH}_3 : \text{C}_6\text{H}_{10}\text{O}$ molar ratio being ≥ 1 , preferably ≥ 1.5 .

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54 Multistep process for the liquid phase ammoximation of carbonyl compounds.

57 Described is a multistep process for the liquid phase ammoximation of carbonyl compounds with H_2O_2 and NH_3 at 60 to 100° C and 1.5 to 5 bar and in the presence of a catalyst based on silicon, titanium and oxygen, wherein:

- in one or more initial steps, the molar ratio H_2O_2 : carbonyl compound ranges from 0.9 to 1.15 and the carbonyl compound conversion is carried out up to at least 95%;
- in a final (exhaustion) step the molar ratio H_2O_2 : carbonyl compound ranges from 1.5 to 3.0.

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The present invention relates to a multistep process for the liquid phase ammoximation of carbonyl compounds with hydrogen peroxide and ammonia. A typical example is the ammoximation of cyclohexanone to cyclohexanone-oxime, and in the following reference will be almost always made to this particular type of process; of course, this does not exclude the applicability of the process according to the invention to other carbonyl compounds.

EP-A-208,311; 267,362; 299,430 and 347,026 teach that said ammoximation can effectively be carried out in the presence of a catalyst based on silicon and titanium. This type of catalyst permits to obtain very high conversions and selectivities; nevertheless, a quantitative conversion (which would simplify the oxime separation and recovery) is practically never obtained, particularly in the case of cyclohexanone, and the unreacted carbonyl compound poses a problem not only because it is necessary to recover it, but also owing to the possible secondary reaction which it can give rise to (during the separation and purification of the oxime). The by-products of these reactions (in the case of cyclohexanone these are cyclohexyl-cyclohexanone, bis-cyclohexenyl-cyclohexanone and octahydro-phenazine), as is known, adversely affect the quality of the caprolactam obtainable in the subsequent Beckmann rearrangement. In order to complete the oximation of the residual ketone, it is possible to resort to a reaction with a solution of hydroxylamine sulphate, under operative conditions known from the art. However, on the one hand, the problem of the non-quantitative conversion of the carbonyl compound is present in both the ammoximation of cyclohexanone to cyclohexanone-oxime and the ammoximation of other ketones and aldehydes such as e.g. acetone, methylethyl ketone (2-butanone), acetophenone, cyclododecanone, enantiic aldehyde (1-heptanal), etc. and, on the other hand, the hydroxylamine sulphate solutions are obtainable only by complex processes such as, for example, the Raschig process (reduction of the nitrogen oxides with ammonium bisulphite).

There has now been found an ammoximation process which permits to reduce the amount of residual ketone (or of residual aldehyde) contained in the effluents of the initial step(s) of the ammoximation process to those levels which can be reached with hydroxylamine sulphate, without resorting, however, to the use of said sulphate which, as already pointed out, can be prepared only by means of quite complex processes.

Accordingly, in its broadest aspect the present invention relates to a multistep process for the liquid phase ammoximation of carbonyl compounds with H_2O_2 and NH_3 , at 60 - 100 °C and 1.5 - 5 bar and in the presence of a (suspended) catalyst based on silicon, titanium and oxygen, wherein:

- a) in one or more initial steps the molar ratio H_2O_2 : carbonyl compound ranges from 0.9:1 to 1.15:1 (preferably from 1.0:1 to 1.1:1) and the carbonyl compound conversion is effected up to at least 95% (preferably up to 96 - 99%);
- b) in a final (last) step (exhaustion step) the molar ratio H_2O_2 : carbonyl compound is at a higher level, i.e., ranges from 1.5:1 to 3.0:1 (preferably from 1.5:1 to 2.2:1).

The above ranges are critical for the purpose of improving the process. It has also been tried to effect the quantitative conversion of the carbonyl compound in a single reactor, without any additional completion (exhaustion) step and by using much higher amounts of oxidant (H_2O_2) already at the beginning, as well as much longer reaction times, but it was found that the initial substantial excess of H_2O_2 and the too long reaction times cause an instability of the reaction system. Namely, competitive reactions were observed, which involved the oxime and/or the carbonyl compound and/or the ammonia. The competitiveness, obviously, refers to the ammoximation reaction. Said competitive (secondary) reactions led to a reduction of the quality of the oxime produced and to a considerable formation of nitrogen-containing by-products (N_2O , N_2 , NO_2^- , NO_3^- etc.). A consequence of this quality reduction was that the quality specifications of the caprolactam obtainable from the oxime (in cascade) were not met. In other words, it has surprisingly been found that it is possible to employ a large excess of H_2O_2 , provided said excess is added only after a certain conversion level has been reached, i.e. provided that the residual carbonyl compound concentrations are very low or, in other words, the carbonyl compound conversion has reached at least 95%. In fact it was observed that under these conditions the expected quality reduction did not occur at all and that a practically complete conversion of the carbonyl compound was obtained without having to carry out the undesired and complex post-treatments (with hydroxylamine sulphate) and without secondary reactions taking place. The practically quantitative reaction of the carbonyl compound provided by the process of the invention results in the production of an oxime of equivalent of higher quality than that obtainable according to the prior art. A few preferred operative details are briefly listed hereinafter.

A) Residual Reagent in the Effluent from the Initial Step(s)

Particularly good results, in terms of yield calculated on hydrogen peroxide and of quality of the oxime produced, may be obtained when the concentration of the residual carbonyl compound in the effluent from the initial step(s) does not exceed 1 and, preferably, 0.5% by weight.

B) Operative Conditions of the Initial Step(s)

The ammonia concentration in the liquid reaction medium preferably ranges from 1.0 to 2.5%

(particularly from 1.5 to 2.0%) by weight. The molar ratio H_2O_2 : ketone (or aldehyde) preferably ranges from 1.0:1 to 1.1:1. The concentration of the catalyst suspended in the liquid medium usually is such as to result in a specific productivity (expressed as parts by weight of oxime produced per part of catalyst and per hour) of from 6 to 12, preferably of about 8. The residence time in each of the initial steps generally does not exceed 120 minutes and preferably ranges from 30 to 90 minutes.

C) Exhaustion Step

In the last step (exhaustion step), where an (almost) complete conversion of the residual carbonyl compound is to be effected, in particular with a concentration of the unreacted compound not higher than 200 ppm (preferably not higher than 100 ppm and, still more preferably, not higher than 50 ppm on the liquid medium), the above parameters, as already mentioned, are in the following ranges:

- molar ratio H_2O_2 : carbonyl compound from 1.5:1 to 3:1 (preferably from 1.5:1 to 2.2:1);
- residence time preferably from 10 to 60 minutes.

It is preferred to not introduce further fresh ammonia in the exhaustion step since the amount dissolved in the liquid is sufficient for the above purpose; too large an ammonia excess, referred to the carbonyl compound, in the presence of a hydrogen peroxide excess could result in a loss of oxidant and in the formation of undesired gaseous by-products, such as N_2 and N_2O . In the exhaustion step, the specific catalyst productivity usually decreases to a lower level, i.e., from 0.1 to 5 (preferably from 0.3 to 0.5), due to the different operative conditions, and the temperature is preferably maintained at the value specified above for the initial step(s).

D) General Considerations

As already mentioned, the temperature in all of the steps ranges from 60 to 100 °C (preferably from 70 to 90 °C). At lower temperatures the reaction is rather slow while at higher temperatures the negative effect of the parallel reactions as well as of the consecutive reactions (which start from already formed oxime) begins to become noticeable. The pressure in each of the initial step(s) and in the exhaustion step is to prevent the reaction liquid to start boiling and is to maintain the ammonia concentration in the liquid medium at from 1 to 2.5% by weight, preferably at a value lower than 2%. The pressure also acts as motive power in the liquid filtration. Pressures of from 1.5 to 5 bar (preferably from 1.8 to 3 bar) are sufficient, with the pressures decreasing from the first to the last step. The residence time in each step, with exception of the last step, is to be such as to result in a residual ketone or residual aldehyde conversion of equal to or higher than 95%. The reaction time, in each of these steps, is generally not longer than one hour in order to prevent subsequent reactions of the oxime which has formed. Conversely, too short reaction times lead to an unsatisfactory conversion of the carbonyl compound and to too high a concentration of the reagent in the liquid medium, which promotes the formation of by-products through condensation reactions. In the last step (exhaustion step), the reaction time usually is much shorter in consideration of the lower amount of ketone (aldehyde) to be converted. The molar ratio hydrogen peroxide/ketone (aldehyde) in each step, with exception of the exhaustion step, preferably is slightly above unity, since a small amount of hydrogen peroxide is always consumed, as already mentioned, in parallel reactions (with formation of gaseous products such as N_2 and N_2O , by ammonia oxidation). Furthermore, as already pointed out, the molar ratio hydrogen peroxide/carbonyl compound in the last step, where it is no longer advisable to feed carbonyl compound and which is to bring the carbonyl compound concentration preferably to values below 200 and particularly below 100 ppm, is considerably higher than that utilized in the preceding step(s) (from 1.5:1 to 3:1 and preferably from 1.5:1 to 2.2:1). The productivity of each step is strictly related to the concentration of the catalyst suspended in the solution contained in each reactor. The continuous feeding to each step is preferably controlled in order to have a specific productivity (expressed in parts of produced oxime per part of catalyst and per hour) within the prefixed values. In order to ensure an effective dispersion of the catalyst in the liquid medium, the catalyst concentration usually ranges from 1 to 15% by weight. At too low a concentration the productivity of each step becomes too low and no profitable in economic respect while too high a concentration gives rise to problems as regards stirring and/or filtration of the reaction product. Preferably and advantageously said concentration is maintained at 1 to 6% by weight. As catalyst it is possible to use, e.g., a titanium silicalite as described in EP-A-267,362 and 299,430, or one of the amorphous compounds described in EP-A-347,926. The average particle size of the catalyst generally ranges from 1 to 100 μm preferably from 5 to 50 μm .

E) solvents

Suitable solvents for the ammoximation (including the exhaustion step) are the usual organic solvents described in the documents mentioned above, a few of which have been cited hereinbefore. Said solvents can be both water-soluble and water-insoluble, provided they are stable (under the reaction conditions) towards hydrogen peroxide and exhibit a good dissolving power towards the oximes, in

particular towards cyclohexanone-oxime. In the case of many oximes it is possible to operate also in an aqueous medium, but cyclohexanone-oxime, owing to its low water-solubility, would tend to deposit on the catalyst, thereby inhibiting the catalyst activity once the saturation limit has been reached. Therefore it is advantageous to use organic solvents in order to obtain a high specific productivity of the catalyst and of the reactor. Suitable solvents are, for example, tertiary alcohols, which are stable to hydrogen peroxide, in particular t-butyl alcohol, miscible in any ratio with water, cyclo-hexanol, and aromatic compounds such as benzene, toluene, xylenes, chlorobenzene, mixtures thereof, etc. If water-immiscible solvents are utilized, the presence of three phases is observed: an aqueous phase (water is produced by the reaction), an organic phase (which maintains in solution most of the oxime produced) and a solid phase which is suspended between the two liquid phases and comprises the catalytic system. In all of the following examples t-butyl alcohol is employed as solvent; however, that does not exclude the possibility of using other solvents which are stable towards hydrogen peroxide (either water-soluble or water-insoluble). Particularly advantageous results may be obtained, for example, by substituting toluene for t-butanol. Due to the low water solubility of cyclohexanone-oxime, it is advisable to limit the amount of water present to that which forms (during the reaction) and to that which probably must be recycled with the solvent. t-Butyl alcohol, for example, which is separated and usually recycled on conclusion of the reaction, has the composition of the aqueous azeotrope (about 12% by weight of water). The oxime concentration gradually rises in each step and its maximum value, when an organic solvent is employed, usually ranges from 10 to 30%, preferably from 20 to 25% by weight. Although it is economically profitable to operate with a maximum oxime concentration this is not too advisable since when said concentration exceeds certain values there is an interference with the subsequent oxime reactions, leading to the formation of by-products which strongly affect the quality thereof. The weight ratio of solvent to carbonyl compound generally ranges from 2.5:1 to 10:1.

F) Operative Details

The process according to the invention and the recovery of the oxime from the solution leaving the last step (exhaustion step), in which the residual carbonyl compound concentration is reduced to a value lower than 200 ppm and even lower than 100 ppm, can be carried out according to the schemes shown in figure 1 and figure 2, which are given for merely illustrative purposes, without limiting, however, the scope of the invention.

According to figure 1, a carbonyl compound, e.g. cyclohexanone (1), hydrogen peroxide (2), ammonia (3) and a t-butanol make-up (now shown in the figure) enter a primary reactor R1, equipped with a stirrer, a filtering element (not shown in the figure) and a venting device (4), where the ammoxidation reaction is effected up to very high values of conversion (up to above 95% of conversion). The reaction mixture (5) is then conveyed into a second step reactor R2 (exhaustion reactor), which also is equipped with a vent (6) and is charged with an excess of hydrogen peroxide (7). The final effluent (8) (practically free of residual carbonyl compound and containing t-butanol, oxime and ammonia) is passed to a distillation column C1. From the column head, the ammonia and all of the solvent (t-butanol in the form of an azeotrope containing 12% by weight of water) are recovered; the ammonia-azeotrope mixture (9) is recycled to the 1st step (primary step). From the bottom of the column C1, a liquid (10) composed of water and oxime is recovered and is then subjected to extraction in an apparatus E fed with toluene (11). All of the oxime migrates to the toluene phase, and from a subsequent separator, not shown in the figure, the toluene phase (12) is withdrawn and sent to a column C2 for solvent distillation and oxime dehydration. From said separator (not shown), a water phase (13), containing most of the water-soluble foreign matters, is discharged. From the head of column C2 toluene is recovered in the form of an azeotropic mixture with the reaction water; after a demixing (not shown in the figure), toluene (11) is recycled to the extraction section. The anhydrous oxime (14) which leaves the bottom of column C2 is passed to the Beckmann rearrangement for the production of, e.g., caprolactam.

Figure 2 illustrates, by means of analogous symbols, the case in which, instead of one primary step, there are two primary steps; figure 3 and figure 4 concern the results of some tests and will be discussed in the examples.

G) Apparatus

The invention can advantageously be carried out in reactors arranged in series and stirred in order to maintain in suspension the catalyst which is insoluble in the liquid medium. The most suitable reactor is that known as CSTR (Continuous Stirred Tank Reactor). This type of reactor ensures an effective dispersion of the catalyst system and at the same time, on the basis of a suitable regulation of the residence times, the desired conversion of the carbonyl compound, the residual concentration of which is to not exceed certain optimum values, beyond which the already cited formation of undesired by-products takes place (which adversely affect the oxime quality and render the oxime not or less

acceptable for the conversion to lactam). Ammonia, hydrogen peroxide and carbonyl compound (in particular cyclohexanone) are continuously fed to each reactor of the initial steps and the temperature is maintained around the desired value (by means of cooling, since the reaction is exothermic). The reaction heat can be removed indirectly (through a heat exchanger arranged inside the reactor) or by causing the reaction liquid to circulate in a refrigerated circuit outside the reactor (loop reactor). Each reactor should be equipped with a vent for removing small amounts of gases (N_2 , O_2 , N_2O) which form as reaction by-products by direct ammonia oxidation. It is advisable to mount on said vent a scrubber for the small amounts of solvent which may be entrained by the gaseous compounds. It also is necessary to install in each reactor a filtering system and a purge for the exhausted catalyst. The filtering system, which is arranged inside the reactor or in a circuit outside the reactor, permits to separate the liquid phase from the catalyst, which remains in the reactor, while the filtered liquid is sent to another reactor or to a distillation column (in the case of the last step) for the oxime recovery. It is preferable to install - coupled to the filtering system - a device for the discontinuous purging of exhausted catalyst, which is to be replaced by a fresh catalyst make-up in order to maintain the desired catalytic activity in each step. The cyclohexanone feeding, however, is not provided for in the last step, since the specific purpose of this step is to complete the conversion of the carbonyl compound. Therefore, the reaction liquid directly flows to the oxime recovery section, without undergoing further treatments. The particle size of the (crystalline or amorphous) catalyst, of the order of tens of μm , permits, on the one hand, an easy dispersion thereof in the reaction medium and, on the other hand, an easy separation, by means of usual filtering systems, from the reaction medium. The following examples are given for merely illustrative purposes and are not to be construed as a limitation of the scope of the invention.

EXAMPLE 1 (COMPARATIVE) - Initial Ammoximation

To a 1 liter reactor, equipped with stirrer and continuous feeding and discharge systems, there were continuously fed:

- cyclohexanone = 70.6 g/h;
- t-butyl alcohol (TBA) (containing about 12% by weight of H_2O) = 232.5 g/h;
- hydrogen peroxide (at 49.7% by weight) = 54.2 g/h (H_2O_2 : ketone feeding molar ratio = 1.10:1);
- gaseous ammonia = amount sufficient to maintain a constant concentration (about 2% by weight calculated on the liquid medium).

The level of the liquid was maintained constant by adjusting an average residence time of 72 minutes (± 1 min), and the catalyst concentration was maintained constant around 2% by weight (calculated on the liquid medium). The catalyst was composed of spheroidal titanium silicalite (suspended in the liquid) having an average particle size of about 20 μm . The reaction temperature was maintained constant at 85°C ($\pm 1^\circ C$) by means of a thermostatic fluid circulating in the reactor jacket; the operating pressure was 2.3 bar. The resulting product was continuously withdrawn through a stainless steel element equipped with a porous baffle and arranged inside the reaction (dimension of the pores = 5 μm), in order to prevent the passage of the catalyst; under regular operating conditions the product leaving the reactor had the following composition:

-	cyclohexanone-oxime	21.0% by weight
-	cyclohexanone	0.3% by weight
-	water	22.0% by weight
-	ammonia	2.0% by weight
-	solvent (TBA)	the balance to 100%.

This corresponded to the following results:

-	cyclohexanone conversion	98.3%
-	cyclohexanone selectivity to oxime	99.6%
-	H_2O_2 conversion	100.0%
-	H_2O_2 selectivity to oxime	89.1%.

Data and results are reported in figure 3 and in Table 1 below, where also the gaseous by-products ($N_2 + N_2O$) and the color (APHA) are indicated. Said APHA color can be determined, as is known, according to ASTM-D-1209/69.

5 EXAMPLE 1/BIS (COMPARATIVE)

Example 1 was repeated, increasing the (H_2O_2 : ketone) feed molar ratio up to a value of 1.15:1. The results, which are reported in Table 1 below and graphically represented in figure 3, show that an increase in the hydrogen peroxide amount results in a small reduction of the product color, while it causes a not acceptable increase of the (gaseous) by-products deriving from ammonia oxidation, in particular of N_2 and N_2O . Conversely, if said ratio is reduced to values below 1.10:1, lower amounts of gaseous by-products, but also much higher (APHA) color values are obtained, as is shown in figure 3, where the amount of by-products is expressed as N l./mole (normal litres per mole of oxime present in the reaction system).

15 EXAMPLE 2 (COMPARATIVE) - Completion of Ammoxidation with Hydroxylamine Sulphate; Integrated Ammoxidation

Example 1 was repeated and the effluent from the reactor was directly fed to an azeotropic distillation column, from the top of which the solvent (t-butanol containing about 12% by weight of H_2O) was recovered; from the bottom there was recovered a mixture having the following composition:

- cyclohexanone-oxime	58.6 % by weight
- cyclohexanone	0.85% by weight
- water	40.5 % by weight

Said tail mixture was continuously fed to a second (stirred) CSTR reactor, to which there was also fed an aqueous solution of hydroxylamine sulphate of formula $(NH_2OH)_2SO_4$, hereinafter referred to as HYXAS, at a concentration of 10% by weight. The hydroxylamine amount was such as to maintain a NH_2OH /cyclohexanone molar ratio of 2/1. The pH was maintained constant at about 4 (± 0.1) by adding an aqueous ammonia solution (at 15% by weight). The temperature was maintained at $90^\circ C$ ($\pm 1^\circ C$).

The average residence time was 15 minutes (± 1 min), thereby obtaining a cyclohexanone-oxime having a maximum concentration of residual cyclohexanone lower than 100 ppm. The effluent from the reactor was sent to a phase separator where (after a residence time sufficient to obtain a sharp phase separation) a molten cyclohexanone-oxime phase, containing 6.5% by weight of water, and an aqueous saline phase were obtained. Said oxime was then dehydrated and subjected to the Beckmann rearrangement; data and results are reported in Table 1.

40 EXAMPLE 3

To a first step (initial ammoxidation step) there were fed, under the operative conditions of example 1:

- cyclohexanone	70.6 g/h
- TBA (12% of H_2O)	232.5 g/h
- hydrogen peroxide (49.7%) (H_2O_2 : ketone feed molar ratio = 1.10:1)	54.2 g/h
- ammonia: amount sufficient to maintain a constant concentration (about 2% by weight) in the liquid medium.	

The effluent from this first step, equal to 300 g/h, having the following composition:

- cyclohexanone-oxime	21.0 % by weight
- cyclohexanone	0.30% by weight
- water	22.0 % by weight
- ammonia	2.0 % by weight

was fed to a second reactor (exhaustion reactor) similar to the first one and maintained at a constant operation pressure of 1.8 bar and at a temperature of 85°C. To said reactor an aqueous solution of hydrogen peroxide at 50% by weight was also fed. The amount of solution was 1.6 g/hour, corresponding to a H₂O₂/residual ketone molar ratio (exhaustion ratio) equal to 2.02:1. Also in this second step (exhaustion step) it was operated with a catalyst in suspension (titanium silicalite) in an amount equal to about 2% by weight of the solution contained in the reactor. The average residence time was 30 minutes (± 1 min). The reaction product leaving the second reactor (through the filtering element) exhibited the following composition:

10	-	cyclohexanone-oxime	21.3% by weight
	-	cyclohexanone	less than 100 ppm
	-	water	23.2% by weight
15	-	ammonia	1.7% by weight
	-	solvent	the balance to 100%.

Considering the total amounts of reagents fed, the H₂O₂/cyclohexanone total molar ratio was 1.13:1. The cyclohexanone conversion was equal to 99.95% and the selectivity of cyclohexanone to cyclohexanone-oxime was higher than 99%. The hydrogen peroxide conversion was practically quantitative and the selectivity of hydrogen peroxide to oxime was 87.4%. After separation of the solvent by distillation and after dehydration of the resulting oxime, there was obtained, by Beckmann rearrangement, a caprolactam satisfying (after purification) the quality specifications required by the market (optical density, at 290 nm, lower than 0.05; permanganate number higher than 20,000 seconds; volatile bases below 0.5 milliequivalents/kg). It is evident that by operating according to the invention it is possible to obtain excellent results without having to utilize a reagent alien to the ammoximation reaction (for example hydroxylamine sulphate). The very small amount of gaseous by-products (0.41 N l./mole) and the final color (about 180 APHA) are graphically represented in figure 4, which permits to immediately recognize the technical importance of the invention. The intersection of the two curves in figure 3 practically indicates an optimum conversion level, beyond which it is advisable to pass to the exhaustion step (with very high H₂O₂ : ketone ratios). It was impossible to foresee the range corresponding to the best results (95-99%).

EXAMPLE 4 - Three-Step Process

35 The reactor of example 1 was fed with

40	- cyclohexanone	35.3 g/h
	- TBA (12% H ₂ O)	232.5 g/h
	- hydrogen peroxide (50%) (H ₂ O ₂ : ketone feed ratio = 1.04:1)	25.5 g/h
	- gaseous ammonia: amount sufficient to maintain constant its concentration (about 2% by weight calculated on the liquid medium).	

45 The liquid level in the reactor was maintained constant and the average residence time was 60 minutes (± 1 min). The catalyst (titanium silicalite) concentration in the reactor was maintained constant (about 2% by weight calculated on the reaction medium). Also the reaction temperature was maintained constant at 85°C (± 1°C), by means of a thermostatic fluid circulating in the reactor jacket; the pressure was equal to 2.8 bar. The cyclohexanone conversion was 97.8%. The composition of the effluent from the first step was as follows:

55	- cyclohexanone-oxime	13.0 % by weight
	- cyclohexanone	0.26% by weight
	- ammonia	2.0 % by weight
	- water	18.2 % by weight.

The product from this first step was passed to a second reactor, identical with the preceding one, and

simultaneously there were fed:

- cyclohexanone	35.3 g/h
- hydrogen peroxide (at 50% by weight) (H_2O_2 : ketone feed ratio = 1.06:1)	26.0 g/h
- gaseous ammonia: amount sufficient to maintain constant its concentration (about 2% by weight).	

The operative conditions of the second step were:

- temperature	85 °C (± 1 °C)
- pressure	2.3 bar
- catalyst in suspension	2% by weight
- average residence time	60 minutes (± 1 min).

The effluent from the second step, equal to 373 g/h, had the following composition:

- cyclohexanone-oxime	21.4 % by weight
- cyclohexanone	0.30% by weight
- ammonia	2.05% by weight
- water	22.1 % by weight.

Said effluent (from the second step) was fed to a third reactor (exhaustion reactor), similar to the reactors of the first and second steps, operating under the following conditions:

- temperature	85 °C (± 1 °C)
- pressure	1.8 bar
- concentration of the catalyst in suspension	about 2% by weight
- average residence time	30 minutes.

Said third reactor was fed with 8 g/h of hydrogen peroxide (at 10% by weight), corresponding to an exhaustion ratio of 2.06:1.

The product of the third step, equal to 380 g/h, had the following composition:

- cyclohexanone-oxime	21.3% by weight
- residual cyclohexanone	less than 100 ppm.

The hydrogen peroxide/cyclohexanone total molar ratio was equal to 1.08:1:

The cyclohexanone conversion was higher than 99.9%.

The cyclohexanone selectivity to cyclohexanone-oxime was 99.4%.

The hydrogen peroxide conversion was quantitative.

The hydrogen peroxide selectivity to oxime was 91.7%.

EXAMPLE 5

Under the operative conditions of example 1, a 2 liter reactor was fed with:

<ul style="list-style-type: none"> - cyclohexanone - t-butyl alcohol (12% H₂O) - hydrogen peroxide (50% by weight) 	133.75 g/h 491.2 g/h 90 g/h
(hydrogen peroxide/ketone feed molar ratio = 0.97:1)	
- gaseous ammonia: amount sufficient to maintain constant its concentration (about 2% by weight on the liquid medium).	

The effluent, equal to 752 g/h, having the following composition:

- cyclohexanone-oxime	19.4% by weight
- cyclohexanone	0.9% by weight
- water	20.1% by weight
- ammonia	2.0% by weight

was passed to an exhaustion reactor of 1 liter volume, operating under the following conditions:

- temperature	85 ° C
- pressure	1.8 bar
- residence time	32 minutes
- suspended catalyst (calculated on the reaction medium)	2% by weight.

To the exhaustion reactor there were also fed 44 g/h of hydrogen peroxide at 10% by weight (hydrogen peroxide/ketone molar ratio = 1.87:1). The product leaving the reactor had the following composition:

- cyclohexanone-oxime	19.3% by weight
- cyclohexanone	200 ppm
- water	24.0% by weight
- ammonia	1.5% by weight.

The total hydrogen peroxide/cyclohexanone molar ratio was 1.6:1.

The cyclohexanone conversion was higher than 99.9%.

The ketone selectivity to oxime was equal to 99.3%.

The hydrogen peroxide conversion was quantitative.

The hydrogen peroxide selectivity to oxime was equal to 93%.

T A B L E 1

EXAMPLES	(H ₂ O ₂ /ketone) feed ratio (***)	Oxime (%)	Residual ketone	HYXAS addition	Final ketone	Ketone conversion (%)	N ₂ N ₂ O (****)	Color (APHA)
1 (*)	1.10:1	21	0.30%	no	0.30%	98.3	0.33	180
1/bis (*)	1.15:1	n.d.	n.d.	no	n.d.	99.0	0.50	110
2 (*)	1.10:1	21	0.85% (**)	yes	less than 100 ppm	n.d.	n.d.	n.d.

(*) Comparative

(**) After distillation of the solvent

(***) Molar ratio of hydrogen peroxide (100%) to ketone

(****) Normal litres per gram mole of oxime contained in the reaction mixture

n.d. not determined

TABLE 2

EXAMPLES	a	c	d	e	f	g	h	i
	Fed ketone (g/h)	Fed hydrogen peroxide (g/h)	H ₂ O ₂ : ketone feed ratio	Oxime in the effluent (%)	Residual ketone in the effluent (%)	H ₂ O ₂ :ketone exhaustion	Final ketone	Total ratio
1st STEP (primary)	70.6	54.2	1.1:1	21.0	0.3	=	=	=
2nd STEP (exhaust.)	=	1.6	=	21.3		2.02:2	less than 100 ppm	1.13:1
1st STEP	35.3	25.5	1.04:1	13.0	0.26	=	=	=
2nd STEP	35.3	26.0	1.06:1	21.4	0.30	=	0.3	=
3rd STEP (exhaust.)	=	8.0	=	21.3	=	2.06:1	less than 100 ppm	1.08:1
1st STEP	133.75	90	0.97:1	19.4	0.9	=	=	=
2nd STEP (exhaust.)	=	44	=	19.3	=	1.87:1	200 ppm	1.06:1

(**) Molar ratio of hydrogen peroxide (100%) to ketone fed to the same step

(***) Total molar ratio of hydrogen peroxide (100%) and ketone fed to all steps

55 Claims

1. A multistep process for the liquid phase ammoximation of carbonyl compounds with H₂O₂ and NH₃ at 60 to 100 °C and 1.5 to 5 bar and in the presence of a catalyst based on silicon, titanium and oxygen,

wherein

a) in one or more initial steps the molar ratio H_2O_2 : carbonyl compound ranges from 0.9:1 to 1.15:1 (preferably from 1.0:1 to 1.1:1) and the carbonyl compound conversion is effected up to at least 95%, preferably up to 96 to 99%;

b) in a final step (exhaustion step) the molar ratio H_2O_2 : carbonyl compound ranges from 1.5:1 to 3.0:1, preferably from 1.5:1 to 2.2:1.

2. The process of claim 1, wherein

- the number of initial steps is 1 or 2; and/or
- the catalyst is titanium silicalite; and/or
- the residual carbonyl compound concentration in the effluent from the initial step(s) is equal to or lower than 1% (preferably $\leq 0.5\%$) by weight; and/or
- the ammonia concentration in the liquid reaction medium of all steps ranges from 1.0 to 2.5, preferably from 1.5 to 2.0% by weight; and/or
- the specific productivity in the initial step(s) ranges from 6 to 12 parts by weight of oxime per part of catalyst and per hour.

3. The process of any one of claims 1 and 2, wherein the temperature ranges from 70 to 90°C, the pressure ranges from 1.8 to 4 bar and the catalyst concentration ranges from 1 to 15% by weight, preferably from 1 to 6% by weight.

4. The process of any one of claims 1 to 3, wherein the specific productivity in the last step (exhaustion step) ranges from 0.1 to 5, preferably from 0.3 to 0.6 parts by weight of oxime per part of catalyst and per hour.

5. The process of any one of claims 1 to 4, conducted in the presence of an organic solvent preferably selected from t-butanol and toluene, the weight ratio of said solvent to said carbonyl compound ranging from 2.5:1 to 10:1.

6. The process of any one of claims 1 to 5, wherein the maximum oxime concentration in the liquid reaction medium ranges from 10 to 30% by weight, preferably from 20 to 25% by weight.

7. The process of any one of claims 1 to 6, wherein the catalyst particles suspended in the reaction liquid have an average size of from 1 to 100 μm preferably of from 5 to 50 μm .

8. The process of any one of claims 1 to 7, wherein the carbonyl compound is selected from cyclohexanone, acetone, methyl ethyl ketone, acetophenone, cyclododecanone and enantiomeric aldehyde.

9. The process of any one of claims 1 to 8, wherein the oxime is recovered from the reaction liquid, after the exhaustion step, by means of azeotropic distillation, followed by extraction with organic solvents, preferably toluene.

10. The process of any one of claims 1 to 9, wherein the reactor for each step is of the CSTR type and is equipped with a porous filtering element, the pores of which have an average size lower than the average size of the catalyst particles.

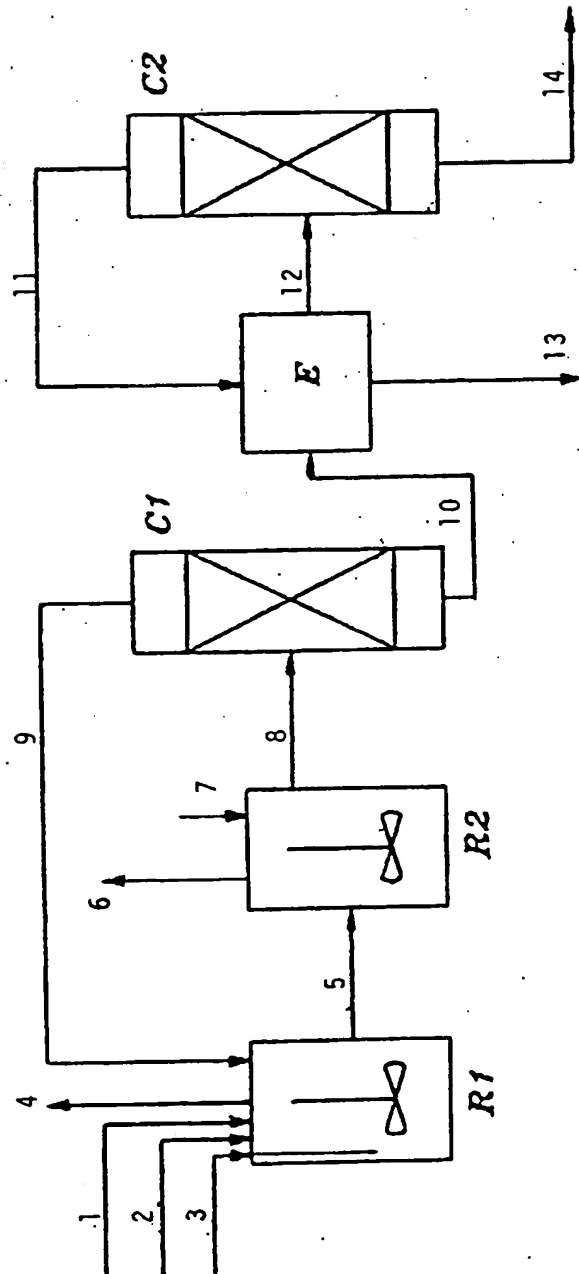


FIG. 1

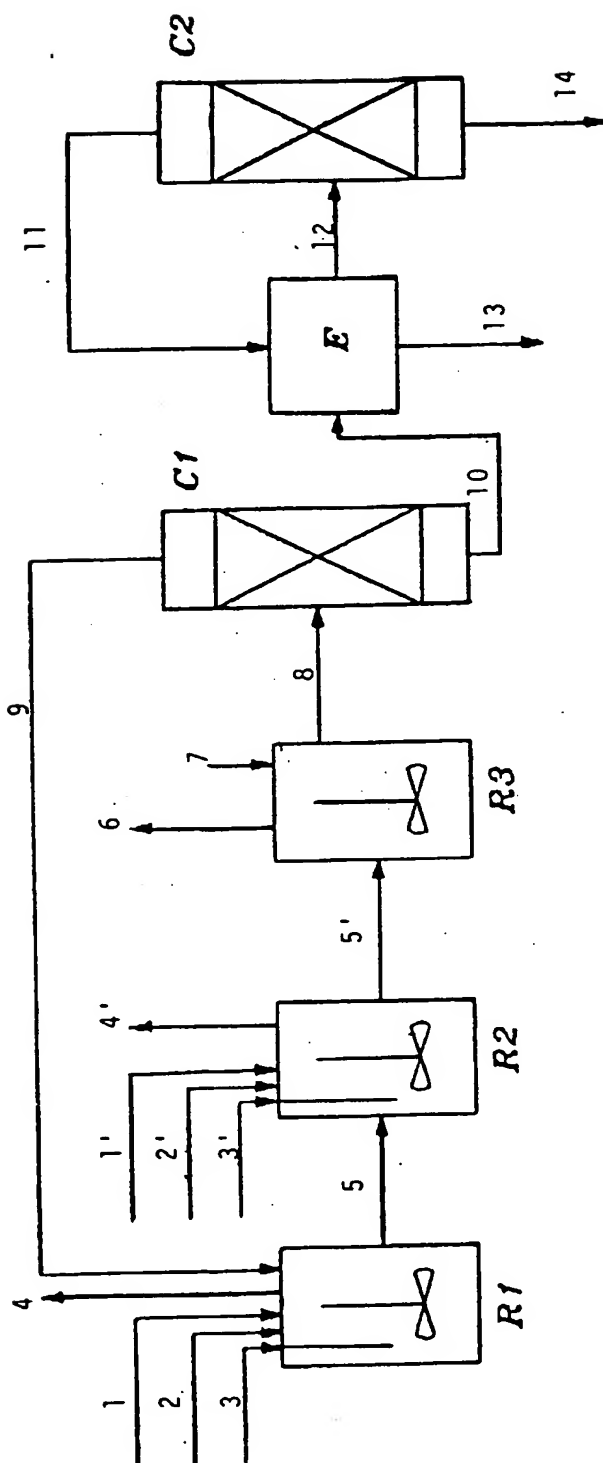


FIG. 2

FIG. 3

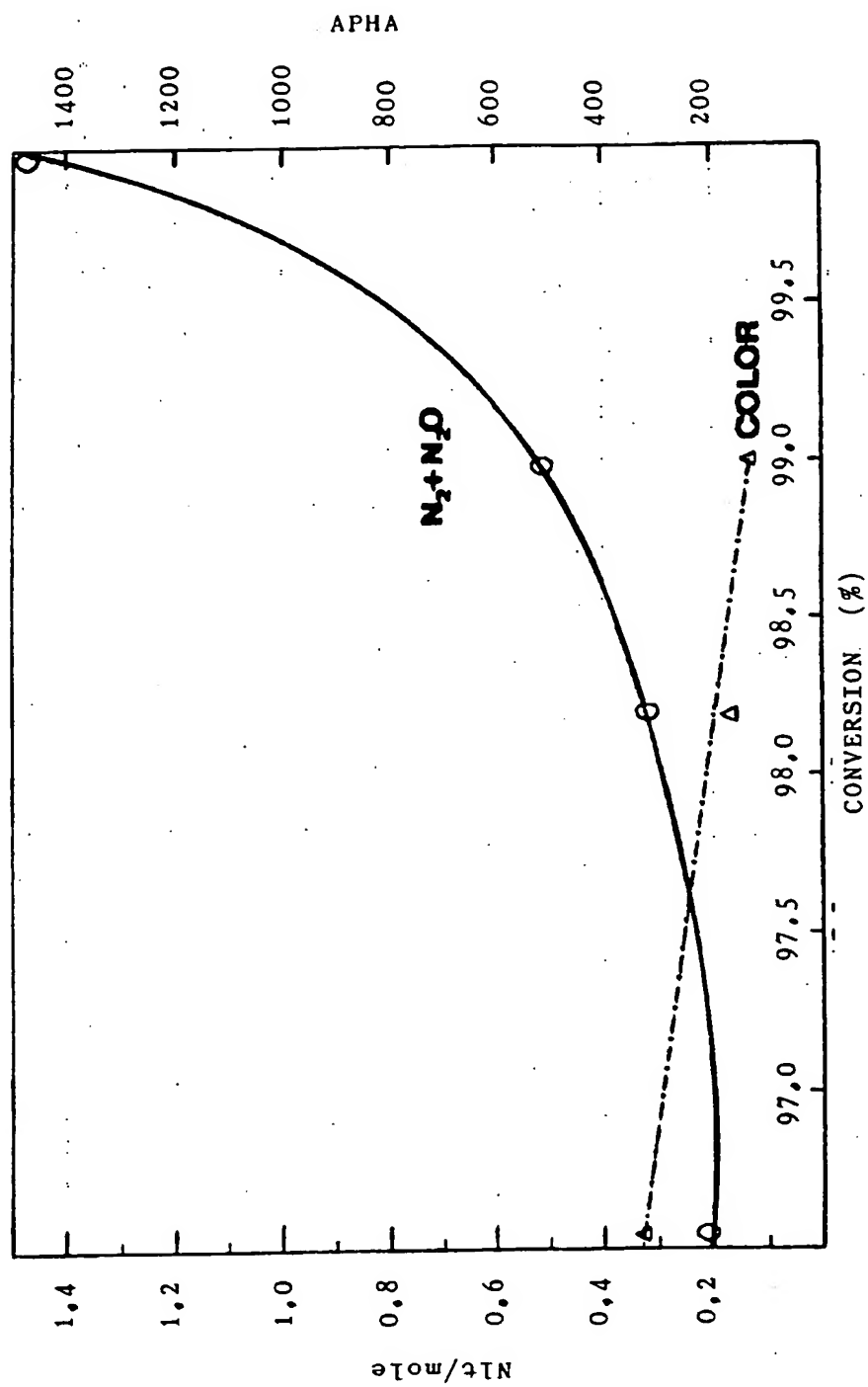
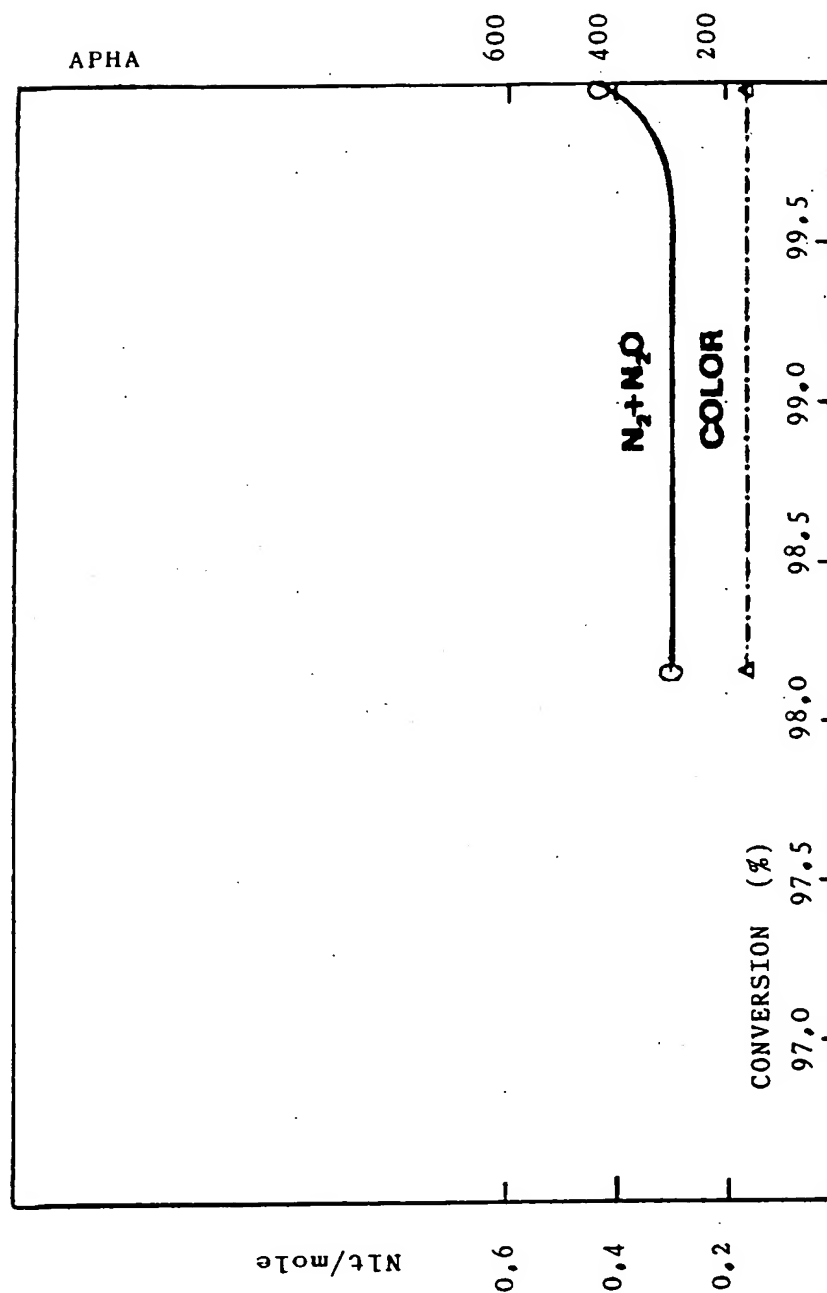


FIG. 4





European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 92 10 1028

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A, D	EP-A-0 267 362 (MONTEDIPE) * claims *	1-10	C07C249/04
A, D	EP-A-0 299 430 (MONTEDIPE) * claims *	1-10	
A, D	EP-A-0 347 926 (MONTEDIPE) * claims *	1-10	
A	EP-A-0 384 390 (MONTEDIPE) * claims *	1-10	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C07C
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 04 MAY 1992	Examiner SANCHEZ Y GARCIA J.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			
T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons A : member of the same patent family, corresponding document			

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54 **Process for preparing a catalyst for the ammoximation of carbonylic compounds.**

57 The present invention relates to a process for preparing a catalyst for the ammoximation of carbonylic compounds, comprising a synthetic, crystalline and porous material based on silicon and titanium oxides, characterized in that a preformed matrix of amorphous silica is impregnated with an aqueous solution containing a titanium compound and an organic nitrogen compound and that the thus impregnated material is provided with a zeolitic structure by means of a usual hydrothermal synthesis, shape and size of the matrix being maintained substantially unchanged thereby.

EP 0 299 430 A1

PROCESS FOR PREPARING A CATALYST FOR THE AMMOXIMATION OF CARBOXYLIC COMPOUNDS

The invention relates to a process for preparing a silicon and titanium containing catalyst showing a zeolitic structure which is particularly suitable for the ammoximation of carboxylic compounds in trickle bed reactors.

From DE-A-1,245,371 It is known to obtain cyclohexanone oxime by catalytic reaction in the liquid phase of cyclohexanone with ammonia and hydrogen peroxide ("ammoximation reaction"), at a temperature from 5 to 40° C and with suitable reactant ratios in the presence of a catalyst consisting of phospho-tungstic acid or similar compounds. However, a drawback of this method is that this type of catalyst is difficult to handle, particularly during the separation of the product from the catalyst. EP-A-208,311 teaches that an effective alternative is the catalysis by a synthetic, crystalline, porous material based on silicon and titanium oxides (titanium-silicalite); in this connection see also US-A-4,410,501 and EP-A-132,550 and 190,609. It has also been found that a special type of titanium-silicalites (post-treated with H₂O₂) shows exceptional and astonishing catalytic properties in the ammoximation reaction of various carboxylic compounds (see EP-A-87 108 577) and that the thus activated titanium-silicalites can be used in continuous operations, both in an isothermal suspended-bed reactor, equipped with stirring means, and in an adiabatic trickle bed reactor. Titanium-silicalites can be prepared by starting from several titanium sources (e.g., tetra-ethyl ortho-titanate, tetra-isopropyl ortho-titanate or peroxy-titanates, optionally formed in situ etc.) and from several silicon sources (tetra-ethyl ortho-silicate, silica sol etc.) The product obtained downstream the hydrothermal synthesis and the subsequent thermal treatments and activation treatments with H₂O₂ is microcrystalline. If the ammoximation process has to be accomplished in a trickle-bed reactor, a careful shaping of the catalyst is necessary. This can be done in further steps, such as pugging the titanium-silicalite with a suitable binding agent and then giving the mixture the shape of spheres, pellets, extrudates (optionally polylobate extrudates, having helical or non-helical grooves) etc. An object of the present invention is to provide a process which allows to obtain titanium-silicalite based catalysts directly in spherical, pellet or extrudate shape, in a much simpler way.

In its broadest aspect, the present invention relates to a process for preparing a catalyst comprising a synthetic crystalline, porous material based on silicon and titanium oxide, particularly suitable for the ammoximation of carboxylic compounds in trickle-bed reactors, characterized in that

a preformed matrix of amorphous silica is impregnated with an aqueous solution containing a titanium compound and an organic nitrogen compound which acts as templating agent, and that the thus impregnated material is provided with a zeolitic structure by means of a usual hydrothermal synthesis, shape and size of the silica matrix being substantially preserved. The amorphous silica matrix may comprise spheres, extrudates (e.g. polylobate extrudates, optionally showing helical grooves) or silica pellets, in the normally available types and sizes. Silica types having a surface area of from 80 to 160 m²/g, a pore volume of from 0.5 to 1.5 cm³/g, in the form of extrudates having a diameter from 1 to 10 mm, preferably from 3 to 6 mm, have proved to be particularly suitable.

As a titanium source, several water-soluble compounds can be used, such as e.g., alkyl titanates, TiOCl₂, peroxytitanates (optionally formed in situ), diisopropyl-bis-triethanolamine titanate and so forth; the Si:Ti molar ratio in the catalyst is advantageously at least 30 and, preferably, 50. Tetrapropylammonium hydroxide can be considered as one of the most widely used templating compounds.

Very good results are obtained by impregnating preformed amorphous silica, dried at temperatures of from 100 to 350° C, according to the dry-impregnation technique, described e.g. in IND. ENG. CHEM. PROD. RES. DEV., Volume 20 (1981), page 441.

The thus impregnated preformed and solid material is transferred to an autoclave and is kept therein at a temperature of from 150 to 200° C preferably (approximately) 175° C and under its autogenous pressure, for from 2 to 20 days, preferably from 3 to 11 days. At the end of the hydrothermal synthesis, the solid material, which retains the shape and size of the silica used as the starting material, is washed with H₂O up to neutral pH and is dried at e.g. 120-130° C for 15 hours. Thereafter it may optionally be calcined (for instance at 430° C for 10 hours).

The best yields are obtained by subsequently employing an activating washing step with an aqueous solution of hydrogen peroxide, optionally in the presence of an acid having a pK of equal to or lower than 5, preferably selected from sulphuric, phosphoric and hydrochloric acid, or in the presence of at least 10 kg of NH₃ per 100 kg of solution.

The catalysts prepared according to the invention were successfully used in continuous runs, for many hours, and with no indication of decay, for the ammoximation of various carboxylic com-

pounds, such as e.g. acetone, cyclohexanone, methyl-ethyl-ketone (butan-2-one), acetophenone or cyclo-dodecanone, with H_2O_2 and NH_3 . Particularly good results are obtained when the ammoximation is preceded by an activating washing of the catalyst, as disclosed e.g. in EP-A-87 108 577. The thus obtained catalyst can be used in trickle-bed reactors, provided with surfaces resistant to hydrogen peroxide.

The conversion to oxime can be carried out at a temperature of from 25 to 100°C (preferably of from 40 to 90°C, and particularly of from 60 to 90°C); tests carried out at 15°C gave poor results. The reaction can be carried out under atmospheric pressure, or under slightly higher pressure, in order to keep dissolved in the reaction medium at least the amount of ammonia which is required for the ammoximation. The H_2O_2 : carbonylic compound molar ratio generally ranges from 0.3 to 2.5 and preferably from 0.5 to 1.5. " H_2O_2 " is intended to mean 100% pure hydrogen peroxide (dilution water excluded). The NH_3 : carbonylic compound molar ratio is equal to or higher than 1 (preferably 1.5), otherwise disturbing parallel reactions may take place. The reaction medium may comprise water or an organic solvent; exceptionally good results were obtained by using as the solvent tert.-butyl alcohol and/or cyclohexanol, optionally mixed with dioxane or toluene. The tert.-butanol (and/or cyclohexanol) : carbonylic compound molar ratio should generally be from 0.1 to 100. Maintaining the hourly space velocity within the range of from 0.1 to 200 kg/hour (preferably from 2 to 200 kg/h) of ketone per kg of pure catalyst (binding agent excluded), and feeding the ketone as a mixture with the organic solvent e.g. tert.-butanol (and/or cyclohexanol), is recommended.

The following examples serve to illustrate the invention.

Example 1

(Syntheses of Titanium-Silicalite in Extrudate Form)

0.6 g of tetraisopropyl ortho-titanate were hydrolysed with 10 ml of deionized water under stirring and at room temperature, thus forming a white gel-like suspension, to which 20 ml of hydrogen peroxide (30% by weight) were added. To the resulting clear solution of orange colour there were added 30 ml of an aqueous tetrapropylammonium hydroxide solution (20% by weight) and the thus obtained clear solution was concentrated by evaporation to a volume of 20 ml. 30 g of

extrudates (solid cylinders of 4 mm of diameter), consisting of amorphous silica having a surface area of 120 m^2/g and a pore volume of 1.1 cm^3/g , were fed into a rotary flask kept under vacuum. The above solution was slowly poured onto the extrudate, while maintaining the vacuum inside the flask. The thus impregnated extrudates were transferred to an autoclave and subjected to a hydrothermal synthesis at 175°C for 9 days under autogenous pressure. At the end, after cooling, the obtained solid, still in the form of extrudates, was washed for an extended period of time to neutral pH with deionized water, dried at 120°C for 15 hours and then calcined at 430°C for 10h. The elemental analysis showed that the solid contained titanium, according to an $\text{Ti}/(\text{Ti} + \text{Si})$ atomic ratio = 0.45%; the X-ray diffraction showed the presence of a crystalline product characterized by the typical reflections of titanium-silicalite such as those shown in US-A-4,410,501. The presence of titanium-silicalite was confirmed by the I.R. spectrum, where the typical bands at 960 and 550 cm^{-1} were present (see the above U.S. patent) and by the nitrogen absorption isotherm (BET method).

Example 2

(Catalyst Activation with H_2O_2)

13 g of the product obtained in Example 1 were poured into an aqueous solution prepared from 26 ml of hydrogen peroxide (30% by weight) and 230 ml of diluted sulphuric acid (10% by weight); the resulting mixture was then stirred for 2 hours at 70°C; thereafter the liquid was decanted. This activation was repeated once more with a fresh solution; the extrudates were filtered off from the liquid and washed with deionized water (to neutral pH). The product was finally dried at 120°C for 15 hours and calcined at 550°C for 2 hours.

Example 3

2 g of the catalyst obtained according to Example 1 were fed into a trickle bed reactor charged with 12 ml/h of an organic solution (containing 8.67% by weight of cyclohexanone, 44.53% by weight of tert.-butyl alcohol and 40.80% by weight of water), with 0.66 ml/h of hydrogen peroxide (34% by weight) and with 0.4 litres/h of ammonia gas. At 80°C a cyclohexanone conversion of 35.5% and a corresponding oxim selectivity of 74.8% were obtained.

Example 4

Example 3 was repeated, the catalyst of Example 1 being replaced by the catalyst of Example 2; a cyclohexanone conversion of 37.6% and a corresponding oxime selectivity of 93.6% were obtained.

Example 5

5 g of the catalyst prepared according to Example 1 were fed into a trickle bed reactor charged with 30 ml/h of an organic solution (containing 8.10% by weight of cyclohexanone, 2.64% by weight of H_2O_2 , 40.90% by weight of tert-butyl alcohol and 48.36% by weight of water) and with 1 litre/h of ammonia gas. At 80°C a cyclohexanone conversion of 47.5%, and an oxime selectivity of 79.8% were observed.

Example 6

Example 1 was repeated, a different type of silica being subjected to impregnation, said silica being characterized by a surface area of 90 m²/g and by a pore volume of 0.6 cm³/g, and being in the form of extruded cylinders (diameter 2 mm). For the impregnation there was used a solution which had been concentrated by evaporation to half-volume (with respect to the one of Example 1), the further impregnation procedure being maintained unchanged. The formation of titanium-silicalite was confirmed by X-ray diffraction spectroscopy, I.R. spectroscopy and nitrogen absorption (BET). Also this catalyst proved to be suitable for the ammoximation of carbonylic compounds in a trickle-bed reactor, yielding high oxime selectivities.

Claims

1. Process for preparing a catalyst for the ammoximation of carbonylic compounds, said catalyst comprising a synthetic, crystalline, porous material based on silicon and titanium oxides, characterized in that a preformed matrix of amorphous silica is impregnated with an aqueous solution containing a titanium compound and an organic nitrogen compound which acts as a templating agent, and that the thus impregnated material is provided with a zeolitic structure by means of a conventional hydrothermal synthesis whereby shape and size of the silica matrix are substantially retained.

2. Process according to claim 1, wherein said impregnation is a dry-impregnation.

3. Process according to any of the claims 1 and 2, wherein said matrix comprises extruded granules (extrudates).

4. Process according to claim 3, wherein said extruded granules have a polylobate shape, optionally showing helical grooves.

5. Process according to any of the preceding claims, wherein said hydrothermal synthesis is followed by a thermal treatment at a temperature of equal to or lower than 430°C preferably 130°C, and by a subsequent activating washing step using an aqueous hydrogen peroxide solution.

6. Process according to claim 5, wherein said washing is carried out in the presence of an acid having a pK of equal to or lower than 5, preferably selected from sulphuric, phosphoric and hydrochloric acid.

7. Process according to claim 5, wherein said aqueous H_2O_2 solution contains at least 10 kg of NH_3 per 100 kg of solution.

8. Process according to any of the preceding claims, wherein the ratio of the silica source to the titanium source is such that the Si:Ti molar ratio, in the finished catalyst, is equal to or larger than 30, and, preferably, 50.

9. Process according to any of the preceding claims, wherein the titanium compound used as the starting material is selected from alkyl-titanates and peroxy-titanates, optionally formed in situ.

10. Catalyst for the ammoximation of carbonylic compounds, obtainable by the process of any of claims 1 to 9.

11. Use of the catalyst according to claim 10 for the ammoximation of carbonylic compounds, preferably selected from acetone, methyl-ethyl-ketone, cyclohexanone, cyclododecanone and acetophenone.

12. Use according to claim 11, wherein said catalyst is continuously exploited inside a trickle-bed reactor.



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EUROPEAN SEARCH REPORT

Application Number

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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
D, P A	EP-A-0 267 362 (MONTEDIPE)		B 01 J 29/04 C 07 C 301/04 C 07 C 301/00
A	EP-A-0 077 522 (HOESCHT)		
A	EP-A-0 111 700 (HOESCHT)		
A	FR-A-2 471 950 (SNAMPROGETTI)		
D, A	EP-A-0 208 311 (MONTEDIPE)		
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			B 01 J C 07 C
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 09-09-1988	Examiner THION M.A.
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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I-20121 Milano (IT)(54) **Two-step process for liquid-phase production of oximes.**

- (57) Two-step process in the liquid phase for producing oximes at 60 - 100 °C and 1.5 - 5 bars, which comprises:
- (a) in a primary step, ammoximating a carbonylic compound with H₂O₂ and NH₃ in the presence of a silicon, titanium and oxygen based catalyst;
 - (b) oximating the residual carbonylic compound with a solution of hydroxylamine, obtained in its turn by oxidizing ammonia with H₂O₂, having a concentration comprised within the range of from 0.01 to 3%, preferably of from 0.5 to 2% by weight, in such a way as to have a molar ratio of hydroxylamine to the carbonylic compound comprised within the range of from 0.9 to 3, preferably of from 1 to 2.

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The present invention relates to a two-step process for producing oximes in the liquid phase.

More particularly, the present invention relates to a process for producing cyclohexanone oxime.

U.S. patent No. 4,794,198 and European patent Nos. 208,311; 267,362; 299,430; 347,926; all to the same Applicant's name, teach that the ammoximation of carbonylic compounds can be effectively carried out in the presence of a silicon, titanium and oxygen based catalyst, which makes it possible very high values of conversion and selectivity to oxime to be achieved. Unfortunately, in practice, above all in the case of cyclohexanone, a complete conversion, which would simplify the operations of oxime separation and recovery, is never reached, with the unreacted carbonylic compound constituting a problem not only due to the need for recovering it, but also owing to the side reactions which it may cause during oxime separation and purification.

The byproducts of these reactions (in the case of cyclohexanone: cyclohexylcyclohexanone, bis-cyclohexenylcyclohexanone and octahydrophenazine) are known to cause a worsening of the quality of the caprolactam which can be obtained from the subsequent Beckmann rearrangement.

The problem of the incomplete conversion of the carbonylic compound interests both cyclohexanone ammoximation into cyclohexanone oxime, and the ammoximation of other ketones, or aldehydes such, e.g., acetone, methyl ethyl ketone (2-butanone), acetophenone, cyclododecanone, enantiomeric aldehyde (1-heptanal) and so forth.

In order to complete the ammoximation of the residual carbonylic compound, use might be made of the reaction with a hydroxylamine sulfate solution under operating conditions which are well-known in the art. However, hydroxylamine sulfate solutions can only be obtained by means of complex processes such as, e.g., the Raschig process, based on the reduction of nitrogen oxides with ammonium bisulfite.

The present Applicant found now an oximation process which makes it possible the amount of carbonylic compound present in the effluent streams from the primary step of the ammoximation process, to be decreased down to the same levels which can be reached with hydroxylamine sulfate, anyway without using said sulfate -- which, as said, can only be produced by means of a considerably complex process.

Therefore, the subject-matter of the present invention is a two-step process for producing oximes in the liquid phase, at 60 - 100 °C and 1.5 - 5 bars, which process comprises:

(a) in a primary step, ammoximating a carbonylic compound with H_2O_2 and NH_3 in the presence of a silicon, titanium and oxygen based catalyst;

(b) oximating the residual carbonylic compound with a solution of hydroxylamine, obtained in its turn by oxidizing ammonia with H_2O_2 , having a concentration comprised within the range of from 0.01 to 3%, preferably of from 0.5 to 2% by weight, in such a way as to have a molar ratio of hydroxylamine to the carbonylic compound comprised within the range of from 0.95 to 3, preferably of from 1 to 2.

The ammoximation reaction of the step (a) is carried out in the presence of suitable solvents. Said solvents, which may be either soluble or insoluble in water, are stable, under the reaction conditions, to the action of hydrogen peroxide and are good solvents for the oximes produced. The ratio of the solvent to the carbonylic compound is generally comprised within the range of from 2.5 to 10 by weight.

Examples of suitable solvents for the process according to the present invention are such tertiary alcohols as t-butyl alcohol, or cyclohexanol or aromatic compounds, such as benzene, toluene, xylenes, chlorobenzene, their mixtures, and so forth.

The ammoximation reaction of the step (a) is preferably carried out in such a way as to reach a conversion of the carbonylic compound, which is higher than 95%, generally comprised within the range of from 96 to 99%. In order to achieve this result, the reaction should preferably be carried out with a molar ratio of H_2O_2 to the carbonylic compound comprised within the range of from 0.95 to 1.15, preferably of from 1 to 1.1, and the concentration of ammonia in the liquid reaction media is comprised within the range of from 1 to 2.5%, preferably of from 1.5 to 2% by weight.

The productivity of the primary step is strictly correlated to the concentration of the catalyst suspended in the reaction media.

The concentration of the catalyst should be such as to yield a specific productivity, expressed as parts, by weight, of oxime produced per each part of catalyst per hour, comprised within the range of from 2 to 12, and preferably should be of round 8.

In order to secure an effective dispersion of catalyst throughout the liquid media, the concentration of said catalyst may be comprised within the range of from 1 to 15%, preferably from 1 to 6% by weight. At too low concentrations, the productivity of the primary step becomes too low and disadvantageous from the economic viewpoint, and at too high concentrations problems of stirring and/or reaction product filtration arise.

As the catalyst, titanium silicalite as disclosed, e.g., in European patent Nos. 267,362 and 299,430, or one of the amorphous compounds disclosed in European patent No. 347,926, may be used.

The catalyst is used in a well-dispersed form in the reaction media, as crystals or microspheres, prepared according to the procedure as disclosed in U.S. patent No. 4,701,428.

5 The size of catalyst particles is generally comprised within the range of from 5 to 100 micrometres.

The operating conditions are, for the primary step, a reaction temperature comprised within the range of from 60 to 100 °C, generally comprised within the range of from 70 to 90 °C. At lower temperatures than this range, the reaction kinetics is rather slow, and at higher temperatures the negative effect of both parallel reactions and consecutive reactions becomes to appear.

10 The reaction pressure during the primary step should prevent the reaction liquid media from starting boiling and should keep ammonia concentration in the liquid reaction media at the preestablished values. Furthermore, the reaction pressure acts as the drive force for the operation of filtration of the liquid reaction media. Most usual pressure values are comprised within the range of from 1.5 to 5 bars, and generally of from 1.8 to 3 bars.

15 Usually, the residence time is shorter than 120 minutes and generally is comprised within the range of from 30 to 90 minutes.

The exhaustion reaction of the step (b) is a non-catalytic reaction in which the conversion of the carbonylic compound is brought to its completion, in such a way that said carbonylic compound concentration is lower than 200 ppm, preferably lower than 100 ppm, and still more preferably, lower than 50 ppm.

20 This result can be obtained by bringing the reaction product from the (a) step into contact with a hydroxylamine solution under such conditions as illustrated hereinabove, and keeping the reaction temperature comprised within the range of from 60 to 100 °C, preferably of from 70 to 90 °C, and keeping the reaction pressure at a slightly lower value than in step (a). The reaction times are comprised within the range of from 5 to 60 minutes, preferably of from 10 to 40 minutes.

25 The hydroxylamine solution is obtained by oxidizing ammonia with hydrogen peroxide, in the liquid phase, in the presence of an analogous catalyst to the one used in the primary ammoxidation step. Such a catalyst is constituted by silicon, titanium and oxygen, has an either crystalline or amorphous structure and preferably is selected from titanium silicalite and mixed (amorphous) silica-titania oxides.

30 This type of catalyst is dispersed throughout the reaction media in a finely subdivided form (particle diameter comprised within the range of from 5 to 100 micrometres) in an amount of from 0.1 to 40 parts by weight, preferably of from 1 to 10 parts, per each 100 parts of solution.

The oxidation of ammonia by means of hydrogen peroxide can be accomplished in several ways. One might operate with aqueous ammonia solutions at concentrations comprised within the range of from 1 to 5% by weight, preferably of from 5 to 30%, or with NH₃ gas.

35 Furthermore, the reaction may be carried out either in the absence, or in the presence, of an organic solvent either miscible or immiscible with water, such as C₁-C₆ aliphatic and cycloaliphatic alcohols (e.g., methanol, ethanol, n- or isobutanol, cyclohexanol, and so on), or C₅-C₈ aliphatic or aromatic hydrocarbons, such as, e.g., toluene; good results were obtained by using, as the solvent, a tertiary alcohol, in particular t-butanol or t-amyl alcohol. The ratio (by volume) of the solvent to water present is comprised within the range of from 0.5 to 200, preferably of from 4 to 50.

40 In general, the reaction is carried out with a molar ratio of the reactants to each other (NH₃:H₂O₂) comprised within the range of from 0.5 to 200, preferably of from 0.9 to 160. The reaction temperatures are usually comprised within the range of from 25 to 150 °C and preferably of from 40 to 120 °C, under the autogenous system pressure, or under higher pressures.

45 The process of production of hydroxylamine solution can be carried out semicontinuously (with continuous feed of only hydrogen peroxide) or continuously (with both reactants being fed continuously). The effluent stream from the reaction is constituted by a suspension which must be filtered in order to recover the catalyst, which is recycled back to the reaction.

50 In order to better understand the present invention and to practice it, some illustrative, non-limitative examples are reported.

Example 1

Primary step - Ammoxidation

55 To a reactor of 1 litre of capacity equipped with stirring means and continuous feed and discharge systems, the following:

- cyclohexanone = 70.6 g/h;

- t-butanol (12% H₂O, by weight) = 232.5 g/h;
- hydrogen peroxide (at 49.7% by weight) = 54.2 g/h (feed molar ratio of H₂O₂:ketone = 1.1);
- ammonia gas: a large enough amount in order to keep ammonia concentration at 2% by weight, relatively to the liquid media.

5 were fed continuously.

The level of the liquid media was kept at a constant value, by regulating the average residence time at 72 minutes and the concentration of the catalyst was kept constant at approximately 2% by weight (relatively to the liquid media). The catalyst consisted of titanium-silicalite in microspheroidal form (suspended in the liquid media), with a granulometric distribution comprised within the range of from 5 to 100 micrometres, prepared according to Example 1 of U.S. patent No. 4,701,428. The reaction temperature was kept constant at 85 °C by means of a thermostatic fluid, circulating inside the reaction jacket. The operating pressure was 2.3 bars.

The resulting product was continuously collected through a porous filter stick of stainless steel arranged inside the reactor. Pore size: approximately 5 micrometres.

15 The reactor leaving product (flow rate 380 g/h) had the following composition:

- cyclohexanone oxime	= 21.0% by weight;
- cyclohexanone	= 0.3% by weight;
- water	= 22.0% by weight;
- ammonia	= 2.0% by weight.

which corresponds to the following results:

- cyclohexanone conversion	98.3%
- cyclohexanone conversion to oxime	99.6%
- H ₂ O ₂ conversion	100.0%
- H ₂ O ₂ selectivity	89.1%

Hydroxylamine preparation

35 To a reactor of AISI 316 steel, of 1.2 litres of capacity, equipped with stirring means and heating jacket, under an inert gas atmosphere the following:

- 12 g of catalyst consisting of titanium-silicalite in microspheroidal form, prepared according to Example 1 of U.S. patent No. 4,701,428;
- 400 ml of t-butanol;
- 400 ml of an aqueous solution at 15% by weight of ammonia.

40 were charged.

To the suspension, kept heated at 80 °C, 43.16 g of hydrogen peroxide at 32.44% by weight was added within about 1 minute, with vigorous stirring.

After 1 hour of reaction, the suspension was cooled, discharged and filtered in order to separate the catalyst.

45 The resulting solution had the following composition:

- hydroxylamine	= 0.74% by weight;
- water	= 48.0% by weight;
- ammonia	= 7.0% by weight;
- solvent	= balance to 100.

The yield to hydroxylamine was of 40.7%, based on hydrogen peroxide.

55 The effluents from the primary ammoxidation reactor were fed to a reactor of CSTR (Continuous Stirred Tank Reactor) type, together with those coming from hydroxylamine synthesis.

The amount of hydroxylamine solution fed was such as to keep the molar ratio of NH₂OH:cyclohexanone at about 1.7.

The temperature was kept at 85 °C; the operating pressure was of 2 bars.

The average residence time was of 15 minutes, with a cyclohexanone oxim solution being thus obtained, which contained less than 100 ppm of residual cyclohexanone.

Example 2

Example 1 was repeated with such an amount of hydroxylamine solution being fed to the exhaustion step as to keep the molar ratio of NH_2OH :cyclohexanone at about 1.4.

The average residence time was of 30 minutes, with a cyclohexanone oxime solution being thus obtained, which contained less than 100 ppm of residual cyclohexanone.

Example 3

Example 1 was repeated with such an amount of an aqueous solution containing 1.7% of hydroxylamine, by weight, being fed to the exhaustion step as to keep the molar ratio of NH_2OH :cyclohexanone at about 1.6.

The hydroxylamine solution was prepared by distilling, under the reduced pressure of 333 mbars, the effluent stream from the ammonia oxidation reactor in such a way as to obtain an overhead stream which consisted of unreacted ammonia and water/t-butanol azeotropic mixture.

With an average residence time of 15 minutes, a cyclohexanone oxime solution was obtained, which contained less than 100 ppm of residual cyclohexanone.

Claims

1. Two-step process for producing oximes in the liquid phase, at 60 - 100 °C and 1.5 - 5 bars, which process comprises:
 - (a) in a primary step, ammoximating a carbonylic compound with H_2O_2 and NH_3 in the presence of a silicon, titanium and oxygen based catalyst;
 - (b) oximating the residual carbonylic compound with a solution of hydroxylamine, obtained in its turn by oxidizing ammonia with H_2O_2 , having a concentration comprised within the range of from 0.01 to 3%, preferably of from 0.5 to 2% by weight, in such a way as to have a molar ratio of hydroxylamine to the carbonylic compound comprised within the range of from 0.95 to 3, preferably of from 1 to 2.
2. Process according to claim 1, in which the ammoximation reaction of the step (a) is carried out in such a way as to reach a carbonylic compound conversion of more than 95%.
3. Process according to claim 2, in which the molar ratio of H_2O_2 to the carbonylic compound is comprised within the range of from 0.95 to 1.15, and the concentration of ammonia in the liquid reaction media is comprised within the range of from 1 to 2.5%.
4. Process according to any of the preceding claims, in which the catalyst concentration in the primary step is comprised within the range of from 1 to 15% by weight.
5. Process according to any of the preceding claims, in which the exhaustion reaction of the step (b) is a non-catalytic reaction in which the conversion of the carbonylic compound is brought to completion in such a way that the its concentration of said carbonylic compound is lower than 200 ppm, preferably lower than 100 ppm.
6. Process according to claim 5, in which the reaction product from the step (a) is brought into contact with a hydroxylamine solution with the reaction temperature being kept comprised within the range of from 60 to 100 °C, and the pressure being slightly lower than in step (a).
7. Process according to claim 5 or 6, in which the reaction times are comprised within the range of from 5 to 60 minutes.